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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE. — XLIV.

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BY CHARLES F. MABERY AND LEE SHEPHERD.

AID IN THE WORK DESCRIBED IN THIS PAPER WAS GIVEN BY THE ACADEMY FROM THE C. M. WARREN FUND FOR CHEMICAL RESEARCH.

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INDEX OF REFRACTION OF THE SOLID HYDROCARBONS IN PETROLEUM.*

By Charles F. Mabery and Lee Shepherd.

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One of the most important physical constants of liquids is the index of refraction from which the molecular refraction may be calculated. Of the two forms of apparatus in use for these determinations, the Abbé and Pulfrich refractometers, the latter is in all respects the most convenient. But neither refractometer as constructed permits of the determination of the index of solid bodies, which requires a rise in temperature sufficient to liquify the solid. So far as we are aware no method has been proposed for determining the index of solids. The only method suggested for ascertaining the index of liquids at increased temperatures is that of Brühl (Ber. d. deutsch. Chem. Gesellsch. 24, 286, 1891), which depends on raising the temperature to the desired point by means of a copper bar of peculiar shape, extending to a sufficient distance from the prism to be heated by a lamp. Sufficient heat is applied to the bar to reach the desired temperature over the prism by conduction. A stirer is also attached to insure equal heating of the liquid.

But this method is not satisfactory, especially for solids, since they require temperatures for melting that are difficult to maintain constant by external application without breaking the joint between the prism and the glass cup which holds the liquid. It occurred to us that a more convenient source of heat for melting solids might be supplied by means

* The solid hydrocarbons used in the preparation of this paper were prepared in the work carried on with aid granted by the Academy from the C. M. Warren Fund for Chemical Research.

of an electric current passing through a wire of suitable size to afford the necessary resistance. After numerous experiments that need not be described in detail it was found that the heat from a coil of wire surrounding the glass cup containing the substance, even with a sheet of asbestos interposed, caused such unequal expansion of cup and prism that the lute cracked, causing leaks at the joint. On trying to maintain the desired temperature by a coil of wire placed within the glass cup it was found difficult to regulate the temperature at just the point desired. Finally it was found that a coil of wire surrounding the glass cup could be relied on to raise the temperature nearly to the point desired, and by means of an inner coil the temperature just required for melting could be obtained. German silver wire was found to be more suitable for the coils on account of its rigidity, and the size selected was No. 25 English standard gauge. The arrangement of outside and inside coils, prism, glass cup, and attachment for stirring the melted solid, are shown in the figure.

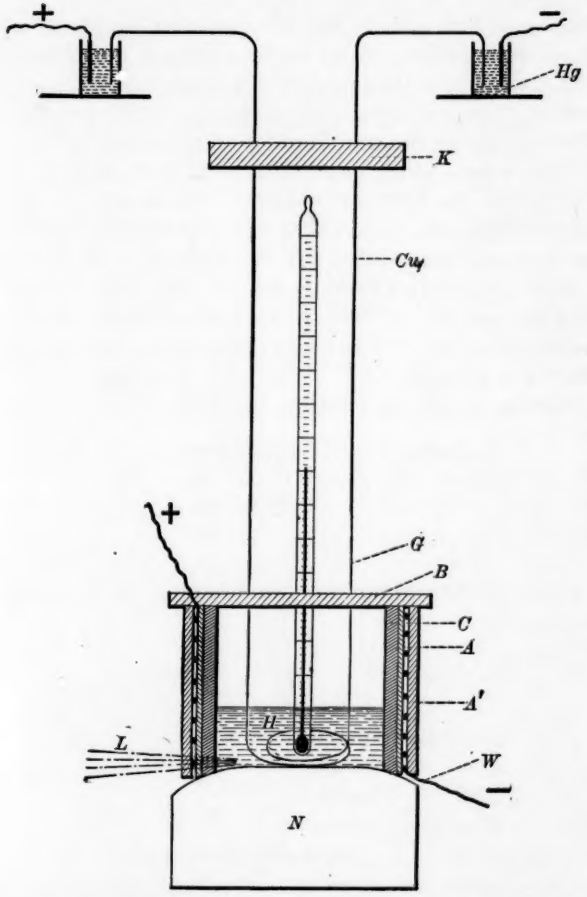
The outer coil of wire W is drawn over a thin sheet of asbestos A which surrounds the glass cup and another thicker sheet is placed outside to prevent radiation. German silver wire of the same size is used for the inner coil and connected above the glass cup to longer copper conductors, which are bent twice so as to dip into mercury cups. This coil is kept in place by means of a cork support K, and the asbestos cover B, which also serves to retain the heat. The inner coil also serves as a stirrer by moving it up and down, which is possible on account of the deep mercury cups. In this manner the solid after melting is very evenly heated. The solid is placed in the glass cup on the face of the prism N, melted by the heated wire, and the temperature kept constant by the inner coil as indicated by the thermometer.

The rays of light L enter the prism through a slit in the asbestos, 0.5 cm. square. A current of 3–5 amperes was sufficient to maintain the temperatures desired in these determinations. With this combination of internal and external heating a temperature of 100° may readily be kept constant without fear of breaking the joint between the prism and glass cup.

The accuracy of this method of heating was determined with water with the following results: —

	20°	30°	40°	50°	60°	70°
Angle,	67° 38′	67° 51′	68° 10′	68° 10′	68° 48′	70° 9′
Index of refraction,	1.3313	1.3304	1.3291	1.3276	1.3241	1.3208
Molecular refraction,	3.692	3.692	3.692	3.692	3.691	3.692

Theoretical molecular refraction of water, 3.692.



This method was applied to the determination of the index of refraction of hydrocarbons separated from Pennsylvania petroleum direct as described by one of us (Mabery) in a former paper, * and also to the same hydrocarbons separated from commercial paraffine. The bodies from crude petroleum had been distilled many times under a tension of 50 mm. and separated from the liquid hydrocarbons by cooling to a low temperature, pressing out the liquid hydrocarbon, and crystallization of the solids from ether and alcohol.

* These Proceedings, XXXII. 365 (1902).

Attempts were first made to ascertain the index directly by melting the solid on the face of the prism; but on account of lack of uniformity in melting, a thin film of the solid persisted on the face of the prism and obstructed the passage of light. The method of mixture was, therefore, resorted to with perfect success. Readings of angles were taken at temperatures above the melting points of the solids and the density of the solids was taken at the same temperatures. The solvent selected was a petroleum distillate with high boiling point, 202°–203°, 50 mm. that had been fractioned many times. It was essentially pure $C_{18}H_{38}$; on account of its high boiling point there was no danger of loss by vaporization during the observations. The index and specific gravity of the solvent were determined at 60°, 70°, and 80°. The specific gravity was in all cases referred to water at 4°.

The following values were given by the solvent oil: —

	Specific Gravity.	Angle of Refraction.	Index of Refraction.
60°	0.7785	49° 6′	1.4341
70°	0.7722	49° 35′	1.4311
80°	0.7612	50° 16′	1.4277

The results of the observations were calculated by the formula for mixtures: —

$$\frac{n-1}{d}\,100 = \frac{n_1-1}{d_1} + \frac{n_2-1}{d_2}\,(100-p)$$

n = index of mixture
n_1 = " " solvent
n_2 = " " solid
d = density of mixture
d_1 = " " solvent
d_2 = " " solid
} all taken at t°
p = per cent of solvent
$(100-p)$ = " " " solid

The mixtures were made of such proportions that each contained approximately 20 % of the solid, and two grams was necessary for each determination, one half the full capacity of the cup, which was necessary to maintain a uniform temperature. The index and specific gravity of each solid were taken at two temperatures, 60° and 70°, or 70° and 80°.

The following results were obtained with the hydrocarbons from Pennsylvania petroleum: —

Distillate, 50mm. 260°–262.° $C_{23}H_{48}$.
Per cent of solvent, 77.86.
" " " solid, 22.14.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
60°	0.7780	0.7769	49° 9′ 3″	1.4337
70°	0.7711	0.7709	49° 43′	1.4304

Calculated for solid:

	n_a.	Molecular Refraction.	Theoretical.
60°	1.4432	110.61	
70°	1.4260	107.68	107.68

Distillate, 50mm. 272°–274.° $C_{24}H_{50}$.
Per cent of solvent, 82.53.
" " " solid, 17.47.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
60°	0.7785	0.7771	49° 5′ 3″	1.4341
70°	0.7734	0.7719	49° 40′	1.4307

Calculated for solid:

	n_a.	Molecular Refraction.	Theoretical.
60°	1.4432	113.08	
70°	1.4251	112.00	112.57

Distillate, 50mm. 282°–284°. $C_{25}H_{52}$.
Per cent of solvent, 84.03.
" " " solid, 15.97.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
70°	0.7724	0.7765	49° 50′	1.4297
80°	0.7618	0.7632	50° 23′ 8″	1.4263

Calculated for solid:

	n_a.	Molecular Refraction.	Theoretical.
70°	1.4241	115.	
80°	1.4212	117.	117.2

Distillate, 50mm. 292°–294°. $C_{26}H_{54}$.
Per cent of solvent, 83.13.
" " " solid, 16.87.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
70°	0.7726	0.7780	49° 38′	1.4309
80°	0.7618	0.7685	50° 13′ 7″	1.4373

Calculated for solid:

	n_α.	Molecular Refraction.	Theoretical.
70°	1.4320	122.	
80°	1.4305	123.2	121.8

Distillate, 50mm. 300°–301°. $C_{27}H_{56}$.
Per cent of solvent, 77.64
" " " solid, 20.36

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
70°	0.7719	0.7757	49° 55′	1.4292
80°	0.7623	0.7655	50° 29′ 4″	1.4257

Calculated for solid:

	n_α.	Molecular Refraction.	Theoretical.
70°	1.4206	124.2	
80°	1.4194	125.45	126.4

Distillate, 50mm. 312°–314°. $C_{28}H_{58}$.
Per cent of solvent, 86.79.
" " " solid, 13.21.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
70°	0.7738	0.7770	49° 40′ 6″	1.4297
80°	0.7618	0.7669	50° 14′ 6″	1.4272

Calculated for solid:

	n_α.	Molecular Refraction.	Theoretical.
70°	1.4184	126.6	
80°	1.4170	128.8	131

Having at hand a series of solid hydrocarbons separated from commercial paraffine, that correspond in composition to the solid hydrocarbons from crude Pennsylvania petroleum, determinations of the indices of refraction of these bodies were made for the purpose of comparison. The formulas of the paraffine hydrocarbons are given as they have been determined, although the results have not been published.

Distillate, 50mm. 260°–262°. $C_{23}H_{48}$.
Per cent of solvent, 79.84.
" " " solid, 20.16.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
60°	0.7780	0.7706	49° 16′ 5″	1.4330
70°	0.7668	0.7641	49° 44′	1.4303

Calculated for solid:

	n_D.	Molecular Refraction.	Theoretical.
60°	1.4256	106.7	
70°	1.4374	111.	108.

Distillate, 50mm. 282°–286°. $C_{25}H_{52}$.
Per cent of solvent, 78.35.
" " " solid, 21.65.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
60°	0.7784	0.7779	49° 10′	1.4337
70°	0.7721	0.7707	49° 46′	1.4301

Calculated for solid:

	n_D.	Molecular Refraction.	Theoretical.
60°	1.4206	117.6	
70°	1.4194	117.	117.2

Distillate, 50mm. 300°–302°. $C_{27}H_{56}$.
Per cent of solvent, 82.81.
" " " solid, 17.19.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
70°	0 7727	0.7770	49° 50′	1.4297
80°	0.7625	0.7669	50° 13′	1.4272

Calculated for solid:

	n_D.	Molecular Refraction.	Theoretical.
70°	1.4287	123.4	
80°	1.4276	126.1	126.4

Distillate, 50mm. 312°–314° $C_{28}H_{58}$.
Per cent of solvent, 79.75.
" " " solid, 20.25.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle of mixture.	n.
70°	0.7737	0.7806	49° 42′	1.4305
80°	0.7630	0.7699	50° 15′	1.4277

Calculated for solid:

	n_D.	Molecular Refraction.	Theoretical.
70°	1.4285	129.3	
80°	1.4226	129.9	131

Commercial Paraffine gave the following indices:
Per cent of solvent, 78.97.
" " " solid, 21.03.

	Sp. gr. of mixture.	Sp. gr. of solid.	Angle for mixture.	n.
60°	0.7784	0.7788	49° 6′ 3″	1.4340
70°	0.7727	0.7732	49° 35′ 6″	1.4311

The results described above show a close agreement in the hydrocarbons separated directly from petroleum, and the corresponding bodies from paraffine, as well as the application of this method for obtaining the molecular refraction of solid bodies.